

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 647 682 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **94115688.7**

(51) Int. Cl.<sup>8</sup>: **C08L 83/07, C08K 3/08,  
C08K 9/06, H01B 1/22**

(22) Date of filing: **05.10.94**

(30) Priority: **06.10.93 JP 274892/93  
06.10.93 JP 274893/93  
17.11.93 JP 311265/93**

(43) Date of publication of application:  
**12.04.95 Bulletin 95/15**

(84) Designated Contracting States:  
**DE ES FR GB IT**

(71) Applicant: **Dow Corning Toray Silicone  
Company, Limited  
Mitsui Bldg. No. 6,  
2-3-16, Nihonbashi-Muromachi,  
Chuo-Ku  
Tokyo 103 (JP)**

(72) Inventor: **Nakayoshi, Kazumi, Dow Corning  
Toray  
Silicone Company, Ltd.,  
2-2, Chigusa Kagan  
Ichihara-shi,  
Chiba Prefecture (JP)  
Inventor: Mine, Katsutoshi, Dow Corning  
Toray  
Silicone Company, Ltd.,  
2-2, Chigusa Kagan  
Ichihara-shi,  
Chiba Prefecture (JP)  
Inventor: Tazawa, Rikako, Dow Corning Toray  
Silicone Company, Ltd.,  
2-2, Chigusa Kagan  
Ichihara-shi,  
Chiba Prefecture (JP)**

(74) Representative: **Spott, Gottfried, Dr.  
Spott, Weinmiller & Partner  
Sendlinger-Tor-Platz 11  
D-80336 München (DE)**

(54) **Silver-filled electrically conductive organosiloxane compositions.**

(57) The electrical properties, particularly contact resistance and volume resistivity, of materials prepared by curing organosiloxane compositions containing finely divided silver as the electroconductive filler surprisingly enhanced by treating the silver particles with an organosilicon compound before incorporating the particles into said compositions.

EP 0 647 682 A1

This invention relates to storage-stable, silver-filled organosiloxane compositions yielding cured electrically conductive elastomers that retain their electrical properties for extended periods of time. The reduced variation of contact resistance and volume resistivity with time exhibited by our elastomers are attributed to the manner in which the silver particles are processed before incorporation into our curable organosiloxane composition.

Elastomers, gels and resins prepared from curable organosiloxane compositions containing finely divided silver particles exhibit high levels of electrical conductivity and are used in specialized applications that require materials exhibiting heat resistance, flex resistance, and electrical conductivity.

The prior art of electrically-conductive, silicone compositions is represented by JP-A 3-170,581 [170,581/91]; JP-A 03-049,105 [049,105/91]; JP-A 59-170,167 [170,167/84]; and US-A 5,227,093.

Several problems are associated with the electrically conductive silicone rubber compositions taught in the publications mentioned. When silver in flake-form is particularly used as a filler, it has been found that during the storage of the composition, the silver flakes separate from the composition, and the composition curability declines with the passage of time. Ultimately, the composition may even become uncureable.

Another problem is that large variations in contact resistance and volume resistivity can occur over time in the cured elastomers prepared from these compositions. This phenomenon can render the rubber unsuitable in use for the continuous connection of electrically conductive elements.

We have now found that one cause of variation in electrical properties of silver-filled organosiloxane elastomers with time is the low affinity of silver particles for the other ingredients of the curable composition used to prepare the elastomer.

We have also confirmed that the curability of these silicone rubber compositions declines with elapsed time due to the presence of residues of the lubricant which is present during grinding of the silver particles. These lubricant residues remain on the surface and/or in the interior of the particles.

One or more of the following lubricants are used with silver particles during this grinding: saturated and unsaturated higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, arachidic acid, and behenic acid; metal soaps such as aluminum laurate, aluminum stearate, zinc laurate, and zinc stearate; higher aliphatic alcohols such as stearyl alcohol; the esters of higher aliphatic alcohols and carboxylic acids; higher aliphatic amines such as stearylamine; higher aliphatic amides; and polyethylene waxes.

Initially, we attempted to remove the lubricant on the surface of the silver particles by subjecting the silver particles to repeated washings with organic solvents. These washings did not provide a satisfactory suppression of the timewise variation in the curability of electrically conductive silicone rubber compositions containing silver particles as a conductive filler.

We have also confirmed that a decline in adhesion and affinity between the cured elastomer and the silver particles contribute to timewise variations in, respectively, the contact resistance and volume resistivity of electrically conductive silicone rubbers.

As a result of our investigations directed at solving the above problems, we have found that the timewise variation in curability can be suppressed by treating silver particles with an organosilicon compound prior to combining said particles with the other ingredients of our curable organosiloxane composition.

We have further found that the presence in our curable compositions of an organosilicon compound containing silicon-bonded alkoxy groups, in addition to the compound used to treat the silver particles, further reduces timewise variations in contact resistance and volume resistivity of the cured elastomer.

The initial aspect of the present invention is achieved by first pretreating the silver particles intended for use in our organosiloxane compositions with an organosilicon compound before the particle is combined with the other ingredients of our compositions.

The variation in electrical properties with time exhibited by our curable composition is surprisingly reduced by the presence in the curable composition of an alkoxy-containing organosilicon compound as an additive. This compound is in addition to any used as the organosilicon compound for treatment of the silver particles. Alternatively, organohydrogensiloxane containing alkoxy groups may function both as the additive and the curing agent for our organosiloxane composition. An organohydrogensiloxane and an organosilicon compound containing silicon-bonded alkoxy groups may also be employed as separate ingredients.

The present invention provides an electrically conductive silicone rubber composition comprising (A) 100 parts by weight of a polyorganosiloxane containing at least two alkenyl radicals per molecule, (B) an organohydrogensiloxane containing at least two silicon-bonded hydrogen atoms in each molecule, in a quantity sufficient to provide from 0.5 to 3 silicon-bonded hydrogen atoms per alkenyl radical present in said polyorganosiloxane,

(C) from 50 to 2,000 parts by weight of finely divided silver particles treated with a first organosilicon compound selected from the group consisting of silanes containing at least one alkoxy group and organosiloxanes; and

(D) from one to 1,000 parts of a platinum group metal per one million parts of the combined weight of (A) and (B) of a hydrosilation catalyst to promote curing of said composition.

In our claimed invention, the silver particles are treated with an organosilicon compound selected from alkoxysilanes and organosiloxanes before combination with the other ingredients of our curable composition.

The variation in electrical properties with time of any cured materials prepared using our curable compositions can be reduced if the compositions contain up to 20 parts by weight of an organosilicon compound containing silicon-bonded alkoxy groups.

The characterizing feature of our curable organosiloxane compositions is the presence therein of silver particles that has been treated with an organosilicon compound before combination with the other ingredients of said composition.

The organosilicon compound, ingredient C, used to treat the silver particles is responsible for the enhanced electrical conductivity exhibited by the silicone rubbers prepared by curing our claimed compositions, irrespective of the storage time of said composition before its use.

The silver particles are prepared by the chemical or electrolytic reduction of a silver compound such as silver nitrate, or by atomization of molten silver. The silver particles to be treated in accordance with the present invention can be 100 percent pure silver or a silver alloy. Useful silver alloys include silver/copper alloys and silver/palladium alloys. The silver alloys may also contain trace amounts of other metals such as zinc, tin, magnesium, and nickel.

With respect to non-metallic impurities on the surface of the treated particles, the organosiloxane composition to avoid cure inhibition of it is particularly preferred that the  $\text{NH}_4^{+2}$  content not exceed 10 ppm and that the  $\text{SO}_4^{-2}$  content not exceed 5 ppm.

While no specific restrictions apply to the diameter of the silver, average particle diameters in the range of from 0.1 to 10 micrometers are preferred. Because the morphology of ingredient C is likewise not critical, the particles can be in the form of granules, dendrites, flakes or the particles may be amorphous. Mixtures of silver particles exhibiting various morphologies can also be used. The flake form of silver is preferred for the preparation of highly electrically conductive cured silicone elastomers.

The organosilicon compound used to treat the surface of the silver particles is not specifically restricted. Examples of suitable treating agents include:

alkoxysilanes such as methyltrimethoxysilane, vinyltrimethoxysilane, 3-glycidoxypolytrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, trimethylethoxysilane, tetramethoxysilane, and tetraethoxysilane;

siloxane oligomers such as silanol-endblocked dimethylsiloxane oligomers, silanol-endblocked dimethylsiloxane/methylvinylsiloxane co-oligomers, silanol-endblocked methylvinylsiloxane oligomers, silanol-endblocked methylphenylsiloxane oligomers, 1,3,5,7-tetramethylcyclotetrasiloxane, and 1,3,5,7,9-pentamethylcyclopentasiloxane;

polyorganosiloxanes ranging from low-viscosity liquids to gums, including

trimethylsiloxy-endblocked polydimethylsiloxanes, trimethylsiloxy-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, trimethylsiloxy-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, trimethylsiloxy-endblocked polymethylhydrogensiloxanes, trimethylsiloxy-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers, silanol-endblocked polydimethylsiloxanes, silanol-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, silanol-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, silanol-endblocked polymethylhydrogensiloxanes, silanol-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers, dimethylvinylsiloxy-endblocked polydimethylsiloxanes, dimethylvinylsiloxy-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, dimethylvinylsiloxy-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, dimethylhydrogensiloxy-endblocked polymethylhydrogensiloxanes, and dimethylhydrogensiloxy-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers; and

silicone resins, including resins composed of  $\text{R}_3\text{SiO}_{1/2}$  and  $\text{SiO}_{4/2}$  units,

silicone resins composed of  $\text{RSiO}_{3/2}$  units, resins composed of the  $\text{R}_2\text{SiO}_{2/2}$  and  $\text{RSiO}_{3/2}$  units, and resins composed of the  $\text{R}_2\text{SiO}_{2/2}$ ,  $\text{RSiO}_{3/2}$ , and  $\text{SiO}_{4/2}$  units.

The organosilicon compounds used to treat the silver particles can be used singly or as mixtures of two or more compounds. The group represented by R in the units of the silicone resins represents any of the substituted and unsubstituted monovalent hydrocarbons discussed in this specification relating to the alkenyl-containing polyorganosiloxane; used as ingredient A.

Silicone resins used as silver treating agents in our invention are preferably solids that soften at above room temperature, most preferably within the range from 50 °C to 150 °C.

The thickness of the coating of the organosilicon compound or a polycondensation product of this compound that is formed during treatment of the silver particles is not critical. The conductivity of cured silicone elastomers prepared from our filled silicone rubber compositions is typically inversely proportional to the thickness of the coating. However, thinner films reduce the affinity between the treated silver particles and the other ingredients of our curable organosiloxane compositions, resulting in larger decreases with the passage of time in the curability of these compositions.

For these reasons, while the optimal coating thickness will be dependent upon the particular end-use application, thicknesses not exceeding 0.1 micrometer are preferred. In order to obtain highly electrically conductive cured silicone rubber, the excess organosilicon compound, or the polycondensation products of this compound, should be removed from the surface of the silver particles by washing the particles with a suitable organic solvent.

The method for treating the silver particles with the organosilicon compound is not critical. As an example, the surface of the silver particles can be wetted with the compound in the absence of any solvent or with a solution of a liquid or solid organosilicon compound in a suitable organic liquid.

Our present treatment method is suitable for silver particles prepared by chemical reduction, electrolytic reduction, atomization, or by other means for the preparation of finely divided particles from molten silver and its alloys.

Chemically reduced silver particles can be prepared, by the reduction of an aqueous silver nitrate solution with a chemical reducing agent such as hydrazine, formaldehyde, or ascorbic acid.

Electrolytically reduced silver, in the form of dendrites, can be deposited on a cathode during the electrolysis of an aqueous silver nitrate solution.

Atomized silver particles can be prepared by spraying molten silver heated to at least 1,000 °C into either water or inert gas.

No specific restrictions apply to the technique for wetting the silver particles with the neat organosilicon compound or solutions of that compound in a suitable organic liquid. Suitable treatment techniques include spraying the silver particles with a neat or solubilized organosilicon compound, immersing the silver particles in a neat or solubilized organosilicon compound, and grinding the silver particles using the neat or solubilized organosilicon compound as a lubricant.

Methods involving grinding are preferred because they produce a flake form of silver that is particularly suitable for preparing highly electrically conductive silicone rubber. The grinding process yields particularly desirable results for the silver flake product. During the grinding of silver particles, the organosilicon compound functions as a surface-treatment agent, and accelerates flake formation by becoming adsorbed onto the activated surface of the flakes. Thus, the aggregation of flakes into larger particles is inhibited.

The device for grinding the silver particles is not critical. Useful devices for this purpose are stamping mills, ball mills, vibratory mills, hammer mills, roll mills, and a mortar and pestle.

The conditions for milling the silver particles are not specifically restricted. They will be dependent at least in part on the diameter and shape of the silver particles. Grinding is preferably conducted while cooling the grinder due to the heat generated during this operation. The silver particles produced by grinding are in the form of flakes that preferably have a diameter in the range of from 0.1 to 10 micrometers.

To facilitate formation of the desired thin coating of the organosilicon compound on the silver particles or when the compound has a relatively high viscosity, the compound(s) used to treat the particles is preferably dissolved in a suitable organic liquid. No specific restrictions apply to organic solvents usable for this purpose. Suitable solvents include alcohols such as methanol, ethanol, and isopropanol; aliphatic compounds such as hexane, heptane, and octane; alicyclic compounds such as cyclohexane and cyclooctane; aromatic compounds toluene and xylene; ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; and esters such as ethyl acetate, and Carbitol™ acetate.

No specific restrictions apply to the conditions for treating the surface of the silver particles with the organosilicon compound during the preparation of ingredient C. Treatment of the particles is preferably carried out at temperatures from ambient to 100 °C, preferably at least 50 °C, for periods from 24 to 150 hours.

To facilitate drying and to also remove excess organosilicon compound adhering to the silver particles, the treated silver particles are preferably washed with a suitable organic solvent, and is then dried for at least 24 hours at temperatures from ambient to 105 °C.

The concentration of the treated silver particles (ingredient C) in the claimed compositions is typically from 50 to 2,000 parts by weight, preferably from 300 to 600 parts, per 100 parts by weight of the